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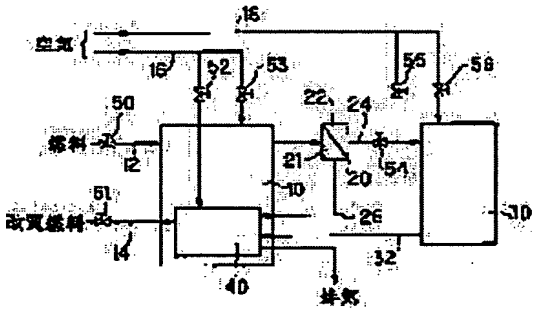
(54) FUEL CELL SYSTEM USING HYDROGEN-SEPARATION FILM AND METHOD FOR MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a fuel cell system and its manufacturing method, using a hydrogen separating film that can completely and easily remove hydrogen within a hydrogen-separation film having it to deteriorate without using a inert gas, when a fuel cell system is stopped and that can control the generation of pressure difference between both poles causing cell components to deteriorate.

SOLUTION: This fuel cell system comprises a reforming apparatus 10 for creating a reformed gas with fuel and air, a hydrogen separation film 20 for separating only hydrogen from the reformed gas, a hydrogen feeding line 24 for feeding a refined hydrogen to a fuel cell 30, an air-feeding line 16 for feeding air to the reforming apparatus, an oxygen-feeding line 18 for feeding oxygen and air to the fuel cell, and a combustor 40 connected to exhaust lines 26, 32 of the hydrogen separating film and the fuel cell, thereby inhibiting fuel from being supplied to the reforming apparatus when the fuel cell system is stopped, closing a switch 54 of the hydrogen feeding line, introducing air into a reformed gas side 21 of the hydrogen separating film and removing hydrogen of the reformed gas side of the hydrogen separating film and a permeating side 22.



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CLAIMS

[Claim(s)]

[Claim 1] The reforming machine which is the fuel cell system generated by making hydrogen, oxygen, or air react, and generates reformed gas from a fuel and air, The hydrogen demarcation membrane which separates only hydrogen from the reformed gas generated with this reforming vessel, The hydrogen supply line which supplies the hydrogen refined from this hydrogen demarcation membrane to a fuel cell, Air supply Rhine which supplies air to a reforming machine, and oxygen supply Rhine which supplies oxygen or air to a fuel cell, While having the combustor connected to exhaust air Rhine of a hydrogen demarcation membrane and a fuel cell and suspending supply of the fuel for a reforming machine at the time of a halt of a fuel cell system The fuel cell system characterized by removing the hydrogen by the side of the reformed gas of a hydrogen demarcation membrane, and transparency by closing the closing motion valve of a hydrogen supply line, and introducing air into the reformed gas side of a hydrogen demarcation membrane.

[Claim 2] The fuel cell system according to claim 1 which makes the hydrogen by the side of transparency of a hydrogen demarcation membrane reverse-penetrate to the reformed gas side of a hydrogen demarcation membrane.

[Claim 3] The fuel cell system according to claim 1 or 2 which permutes the hydrogen in a fuel cell with air at the time of a fuel cell system stop.

[Claim 4] The fuel cell system according to claim 3 the pressure by the side of the fuel electrode of a fuel cell and an oxygen pole was made to become almost equal.

[Claim 5] The control approach of the fuel cell system which is the control approach of the fuel cell system using the hydrogen demarcation membrane generated by making hydrogen, oxygen, or air react, and is characterized by to remove the hydrogen in a hydrogen demarcation membrane by introducing air into the reformed gas side of a hydrogen demarcation membrane, and making the hydrogen by the side of transparency of a hydrogen demarcation membrane reverse-penetrate to the reformed gas side of a hydrogen demarcation membrane at the time of a halt of a fuel cell system.

[Claim 6] While being the control approach of the fuel cell system using the hydrogen demarcation membrane generated by making hydrogen, oxygen, or air react and permuting the hydrogen in a fuel cell with air at the time of a halt of a fuel cell system The control approach of the fuel cell system characterized by removing the hydrogen in a

hydrogen demarcation membrane by introducing air into the reformed gas side of a hydrogen demarcation membrane, and making the hydrogen by the side of transparency of a hydrogen demarcation membrane reverse-penetrate to the reformed gas side of a hydrogen demarcation membrane.
[Claim 7] The control approach of the fuel cell system according to claim 6 which controlled the pressure by the side of the fuel electrode of a fuel cell, and an oxygen pole to become almost equal.

[Claim(s)]
[Claim 1] The reforming machine which is the fuel cell system generated by making hydrogen, oxygen, or air react, and generates reformed gas from a fuel and air, The hydrogen demarcation membrane which separates only hydrogen from the reformed gas generated with this reforming vessel, The hydrogen supply line which supplies the hydrogen refined from this hydrogen demarcation membrane to a fuel cell, Air supply Rhine which supplies air to a reforming machine, and oxygen supply Rhine which supplies oxygen or air to a fuel cell, While having the combustor connected to exhaust air Rhine of a hydrogen demarcation membrane and a fuel cell and suspending supply of the fuel for a reforming machine at the time of a halt of a fuel cell system The fuel cell system characterized by removing the hydrogen by the side of the reformed gas of a hydrogen demarcation membrane, and transparency by closing the closing motion valve of a hydrogen supply line, and introducing air into the reformed gas side of a hydrogen demarcation membrane.
[Claim 2] The fuel cell system according to claim 1 which makes the hydrogen by the side of transparency of a hydrogen demarcation membrane reverse-penetrate to the reformed gas side of a hydrogen demarcation membrane.
[Claim 3] The fuel cell system according to claim 1 or 2 which permutes the hydrogen in a fuel cell with air at the time of a fuel cell system stop.
[Claim 4] The fuel cell system according to claim 3 the pressure by the side of the fuel electrode of a fuel cell and an oxygen pole was made to become almost equal.
[Claim 5] The control approach of the fuel cell system which is the control approach of the fuel cell system using the hydrogen demarcation membrane generated by making hydrogen, oxygen, or air react, and is characterized by to remove the hydrogen in a hydrogen demarcation membrane by introducing air into the reformed gas side of a hydrogen demarcation membrane, and making the hydrogen by the side of transparency of a hydrogen demarcation membrane reverse-penetrate to the reformed gas side of a hydrogen demarcation membrane at the time of a halt of a fuel cell system.
[Claim 6] While being the control approach of the fuel cell system using the hydrogen demarcation membrane generated by making hydrogen, oxygen, or air react and permuting the hydrogen in a fuel cell with air at the time of a halt of a fuel cell system The control approach of the fuel cell system characterized by removing the hydrogen in a hydrogen demarcation membrane by introducing air into the reformed gas side of a hydrogen demarcation membrane, and making the hydrogen by the side of transparency of

a hydrogen demarcation membrane reverse-penetrate to the reformed gas side of a hydrogen demarcation membrane.
[Claim 7] The control approach of the fuel cell system according to claim 6 which controlled the pressure by the side of the fuel electrode of a fuel cell, and an oxygen pole to become almost equal.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the fuel cell system which used the hydrogen demarcation membrane, and its control approach.
[0002]
[Description of the Prior Art] The solid-state polyelectrolyte mold fuel cell (PEFC) with which the fuel cell system by which current and development are furthered is made to react, and generates hydrogen, and oxygen or air is mainly used, and it is usually called for that a generation of electrical energy of a fuel cell stops to a halt of a fuel cell system and coincidence. Moreover, in the case of a solid-state polyelectrolyte mold fuel cell, H2 [one mol] and O2 [1/2-mol] react, and one mol H2O generates. Since the consumption of the hydrogen by the side of the fuel electrode of a fuel cell became large and the pressure by the side of a fuel electrode declined greatly relatively by this as compared with the air by the side of the oxidation pole of a fuel cell (oxygen) at the time of a halt of a fuel cell system, big differential pressure occurred and the trouble that the cell component of a fuel cell will deteriorate was between the fuel electrode side whose electrolyte layer is pinched, and the oxidation pole side.
[0003] In order to cancel these points, in JP,7-272740,A, permuting the reactant gas in a fuel cell (mainly hydrogen) with inert gas (for example, N2 grade) or reacted air is indicated at the time of a fuel cell system stop, and in JP,11-111319,A, in order to prevent waste of inert gas, the system which detects the completion of a permutation by inert gas with a thermo sensor is indicated.
[0004] Moreover, the more the reactant gas used with the above-mentioned fuel cell has the high concentration of the hydrogen which is a principal component, in order to remove CO with a poisoning operation it not only to be able to to raise the generating efficiency of a fuel cell, but, the more the system which supplies purification and the pure hydrogen gas which carried out CO removal to a fuel cell for reformed gas using a hydrogen demarcation membrane is indicated like JP,4-121973,A.
[0005] However, since a hydrogen demarcation membrane would deteriorate if the temperature is lowered under a hydrogen ambient atmosphere when a hydrogen demarcation membrane is applied to a fuel cell system, hydrogen needed to be removed from the inside of a hydrogen demarcation membrane at the time of a fuel cell system stop. For this reason, when including a hydrogen demarcation membrane in the conventional

fuel cell system (refer to JP,7-272740,A and JP,11-111319,A), in order to have to remove hydrogen from both by the side of the reformed gas of a hydrogen demarcation membrane, and transparency, there was a trouble that a fuel cell system became complicated and cost also became high. Moreover, in JP,4-121973,A, consideration was not enough made about making a halt of a fuel cell system and coincidence suspend a generation of electrical energy of a fuel cell.

[0006]

[Problem(s) to be Solved by the Invention] This invention is made in view of this situation, and the place made into the purpose is to offer the fuel cell system using the hydrogen demarcation membrane which can control generating of the differential pressure between the two poles of the fuel cell which causes degradation of the cell component of a fuel cell, and its control approach, without using inert gas at the time of a halt of a fuel cell system while the hydrogen in the hydrogen demarcation membrane constituting the cause of degradation of a hydrogen demarcation membrane is removable certainly and simple.

[0007]

[Means for Solving the Problem] Namely, the reforming machine which is the fuel cell system which is generated by making hydrogen, oxygen, or air react according to this invention, and generates reformed gas from a fuel and air, The hydrogen demarcation membrane which separates only hydrogen from the reformed gas generated with this reforming vessel, The hydrogen supply line which supplies the hydrogen refined from this hydrogen demarcation membrane to a fuel cell, Air supply Rhine which supplies air to a reforming machine, and oxygen supply Rhine which supplies oxygen or air to a fuel cell, While having the combustor connected to exhaust air Rhine of a hydrogen demarcation membrane and a fuel cell and suspending supply of the fuel for a reforming machine at the time of a halt of a fuel cell system The fuel cell system characterized by removing the hydrogen by the side of the reformed gas of a hydrogen demarcation membrane and transparency is offered by closing the closing motion valve of a hydrogen supply line, and introducing air into the reformed gas side of a hydrogen demarcation membrane. As for the hydrogen by the side of transparency of a hydrogen demarcation membrane, at this time, it is desirable to make it reverse-penetrate to the reformed gas side of a hydrogen demarcation membrane.

[0008] In addition, it is desirable to permute the hydrogen in a fuel cell with air in this invention at the time of a fuel cell system stop, and it is desirable to make the pressure by the side of the fuel electrode of a fuel cell and an oxygen pole become almost equal.

[0009] Moreover, it is the control approach of the fuel cell system using the hydrogen demarcation membrane generated by making hydrogen, oxygen, or air react, and, according to this invention, the control approach of the fuel cell system characterized by to remove the hydrogen in a hydrogen demarcation membrane is offered by introducing air into the reformed-gas side of a hydrogen demarcation membrane, and making the hydrogen by the side of transparency of a hydrogen demarcation membrane reverse-penetrate to the reformed-gas side of a hydrogen demarcation membrane at the

time of a halt of a fuel cell system.
[0010] Furthermore, while according to this invention being the control approach of the fuel cell system using the hydrogen demarcation membrane generated by making hydrogen, oxygen, or air react and permuting the hydrogen in a fuel cell with air at the time of a halt of a fuel cell system The control approach of the fuel cell system characterized by removing the hydrogen in a hydrogen demarcation membrane is offered by introducing air into the reformed gas side of a hydrogen demarcation membrane, and making the hydrogen by the side of transparency of a hydrogen demarcation membrane reverse-penetrate to the reformed gas side of a hydrogen demarcation membrane. At this time, it is desirable to control the pressure by the side of the fuel electrode of a fuel cell and an oxygen pole by this invention to become almost equal.
[0011]
[Embodiment of the Invention] The fuel cell system of this invention removes the hydrogen by the side of the reformed gas of a hydrogen demarcation membrane, and transparency by closing the closing motion valve of a hydrogen supply line, and introducing air into the reformed gas side of a hydrogen demarcation membrane at the time of a halt of a fuel cell system, while suspending supply of the fuel for a reforming machine. Thereby, generating of the differential pressure between the two poles of the fuel cell which causes degradation of the cell component of a fuel cell can be controlled, without using inert gas, while the hydrogen in the hydrogen demarcation membrane which causes [of a hydrogen demarcation membrane] degradation at the time of a halt of a fuel cell system is removable certainly and simple.
[0012] Here, in case the main descriptions of the fuel cell system of this invention remove the hydrogen in a hydrogen demarcation membrane, by permuting with air the hydrogen which remains in the reformed gas side of a hydrogen demarcation membrane, they reduce the hydrogen partial pressure by the side of the reformed gas of a hydrogen demarcation membrane, and are in making the hydrogen by the side of transparency of a hydrogen demarcation membrane reverse-penetrate to the reformed gas side of a hydrogen demarcation membrane. Thereby, the hydrogen in the hydrogen demarcation membrane constituting the cause of degradation of the hydrogen demarcation membrane at the time of a temperature fall can be removed certainly and simple only by introducing air into the reformed gas side of a hydrogen demarcation membrane, without establishing a purge line in the transparency side of a hydrogen demarcation membrane.
[0013] Moreover, as for the fuel cell system of this invention, it is desirable to permute the hydrogen in a fuel cell with air at the time of a fuel cell system stop. Generating of the differential pressure between the two poles (a fuel electrode and oxidation pole) of the fuel cell which it not only can suspend a generation of electrical energy of a fuel cell immediately, but causes degradation of the cell component of a fuel cell by this at the time of a fuel cell system stop can be controlled. In addition, as for the pressure by the side of the fuel electrode of a fuel cell, and an oxygen pole, controlling to become almost equal is desirable.

[0014] Furthermore, as for the fuel cell system of this invention, it is desirable as gas for a permutation to use air instead of inert gas. Thereby, since the bomb which stores inert gas is unnecessary, it can contribute to lightweight-izing of a fuel cell system, and reduction of a running cost.

[0015] Hereafter, based on a drawing, this invention is further explained to a detail. Drawing 1 is the outline block diagram having shown an example of the fuel cell system of this invention. The reforming machine 10 with which an example of the fuel cell system of this invention generates reformed gas from a fuel and air as shown in drawing 1 , The hydrogen demarcation membrane 20 which separates only hydrogen from the reformed gas generated with the reforming vessel 10, The hydrogen supply line 24 which supplies the hydrogen refined from the hydrogen demarcation membrane 20 to a fuel cell 30, It has the combustor 40 connected to the reforming machine 10 and the fuel cell 30 in air supply Rhine 16 and 18 which supplies air, and exhaust air Rhine 26 and 32 of the hydrogen demarcation membrane 20 and a fuel cell 30. In addition, a combustor 40 processes surplus hydrogen, oxygen, etc. in exhaust gas by introducing the reforming machine 10, the hydrogen demarcation membrane 20, and the exhaust gas from a fuel cell 30 into the combustion ambient atmosphere of a reforming fuel and air. Moreover, the reforming fuel supply line 14 to a combustor 40 is not necessarily required, and if the operating temperature of the reforming machine 10 is held by combustion of the non-penetrated gas of the reformed gas supplied from exhaust air Rhine 26, it is satisfactory.

[0016] Here, the fuel cell system shown above is performed by the following procedures when stopping a fuel cell system. First, the 5th closing motion valve 54 of the hydrogen supply line 24 is closed, and the hydrogen supply to a fuel cell 30 is suspended at the same time it closes the 1st closing motion valve 50 of the fuel supply line 12 and suspends the fuel supply to the reforming machine 10.

[0017] Next, the function of the reforming machine 10 and a fuel cell 30 is stopped by opening the 4th closing motion valve 53 and the 6th closing motion valve 55, introducing air into reformed gas side 21 of the inside of the reforming machine 10, and the hydrogen demarcation membrane 20, and permuting the hydrogen in the reformed gas in the reforming machine 10, the hydrogen demarcation membrane 20, and a fuel cell 30 with air. Since the hydrogen of transparency side 22 of the hydrogen demarcation membrane 20 is reverse-penetrated to reformed gas side 21 of the hydrogen demarcation membrane 20 by the fall of the hydrogen partial pressure of reformed gas side 21 of the hydrogen demarcation membrane 20 at this time, the hydrogen in the hydrogen demarcation membrane 20 is removable to the hydrogen partial pressure near parenchyma 0. In addition, the exhaust gas discharged from the reforming machine 10, the hydrogen demarcation membrane 20, and the fuel cell 30 is discharged out of a system, after combustion processing is carried out with a combustor 40.

[0018] After closing the 4th closing motion valve 53, the 6th closing motion valve 55, and the 7th closing motion valve 56, the 2nd closing motion valve 51 of the reforming fuel supply line 14 and the 3rd closing motion valve 52 of air supply Rhine 16 are closed, a

combustor 40 is stopped, and a fuel cell system is made to lower finally.
[0019] In addition, the compressor (not shown) connected to the fuel pump (not shown) connected to each closing motion valve 50-56 and the fuel supply line 12, the reforming fuel pump (not shown) connected to the reforming fuel supply line 14, and air supply Rhine 16 and 18 is connected electrically, and these actuation is controlled by the control means (not shown).
[0020]
[Example] Hereafter, although this invention is further explained to a detail using an example, this invention is not restricted to these examples.
(Example) In order to verify the hydrogen removal approach in the hydrogen demarcation membrane in the fuel cell system of this invention, it experimented using the equipment shown in drawing 2 . After installing the hydrogen demarcation membrane 60 in a coil 64 (the product made from stainless steel, content volume: 0.5l.), the coil 64 was heated at 400 degrees C with the electric furnace 62. Next, the bulb V1 was opened and eight atmospheric pressures (gage pressure) and the methanol-reforming simulation gas (hydrogen: 65%, carbon-dioxide:23%, carbon monoxide:2%, 10% of steams) of 6 l/min were supplied in the reactor 64 using the massflow controller M1. In addition, the supply gas line was heated at 130 degrees C at the ribbon heater so that a steam might not condense.
[0021] As a result of measuring a permeated water quantum with a flowmeter M3 at this time, it was 3 l/min and hydrogen recovery was 80%. In addition, bulbs V1, V3, and V4 were in the open condition at the time of the above-mentioned measurement.
[0022] Furthermore, after operating the equipment shown in drawing 2 on the above-mentioned experiment conditions for 1 hour, where a bulb V4 is opened, bulbs V1 and V3 were closed, the bulb V2 was opened, and air was introduced in the reactor 64 by 10 l/min with gage pressure:0.2 atmospheric pressure and the massflow controller M2. When air was introduced in the coil 64 at this time, as a pressure gage P showed, the pressure by the side of transparency of the hydrogen demarcation membrane 60 began to fall, and it almost became zero atmospheric pressure with absolute pressure within 1 min.
[0023] From the above thing, the hydrogen removal in the hydrogen demarcation membrane 60 reduced remarkably the hydrogen partial pressure by the side of the reformed gas of the hydrogen demarcation membrane 60, and checked being carried out by making the hydrogen gas (concentration: about 99% or more) which remained with atmospheric pressure in the transparency side of the hydrogen demarcation membrane 60 reverse-penetrate to the reformed gas side of the hydrogen demarcation membrane 60. In addition, the above-mentioned hydrogen demarcation membrane used for the front face of an alumina porosity base (outer-diameter:17mm and die-length:100mm) (pore size: 0.6 micrometers) what formed 5-micrometer Pd thin film with plating.
[0024]
[Effect of the Invention] The fuel cell system and its control approach of this invention can control generating of the differential pressure between the two poles of the fuel cell which causes degradation of the cell component of a fuel cell while being able to remove the

hydrogen in the hydrogen demarcation membrane constituting the cause of degradation of a hydrogen demarcation membrane certainly and simple, without using inert gas at the time of a halt of a fuel cell system.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the outline block diagram showing an example of the fuel cell system of this invention.

[Drawing 2] It is the outline diagram showing an example of the hydrogen removal experimental device in the hydrogen demarcation membrane in the fuel cell system of this invention.

[Description of Notations]

10 -- A reforming machine, 12 -- A fuel supply line, 14 -- Reforming fuel supply line, 16 -- Air supply Rhine, 18 -- Air supply Rhine (oxygen supply Rhine), 20 -- A hydrogen demarcation membrane, 21 -- A reformed gas side (hydrogen demarcation membrane), 22 -- Transparency side (hydrogen demarcation membrane), 24 [-- Exhaust air Rhine,] -- A hydrogen supply line, 26 -- Exhaust air Rhine, 30 -- A fuel cell, 32 40 [-- The 3rd closing motion valve,] -- A combustor, 50 -- The 1st closing motion valve, 51 -- The 2nd closing motion valve, 52 53 [-- The 7th closing motion valve, 60 / -- A hydrogen demarcation membrane, 62 / -- An electric furnace, 64 / -- A coil, V1-V4 / -- A bulb, M1-M2 / -- A massflow controller, M3 / -- A flowmeter, P / -- Pressure gage.] -- The 4th closing motion valve, 54 -- The 5th closing motion valve, 55 -- The 6th closing motion valve, 56

[Translation done.]

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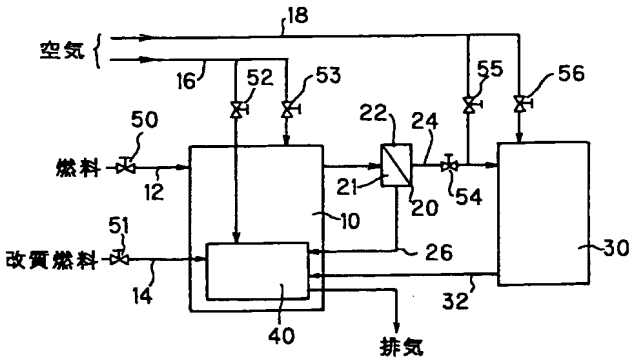
(54)【発明の名称】水素分離膜を用いた燃料電池システム及びその制御方法

(57)【要約】　（修正有）

【課題】　燃料電池システムの停止時に、不活性ガスを用いずに、水素分離膜の劣化の原因となる水素分離膜内の水素を確実且つ簡便に除去でき、電池構成要素の劣化を引き起こす両極間の圧力差の発生を抑制できる水素分離膜を用いた燃料電池システム及びその制御方法。

【解決手段】　燃料と空気から改質ガスを生成する改質器１０と、改質ガスから水素のみを分離する水素分離膜２０と、水素分離膜から精製された水素を燃料電池３０に供給する水素供給ライン２４と、改質器に空気を供給する空気供給ライン１６と、燃料電池に酸素又は空気を供給する酸素供給ライン１８と、水素分離膜及び燃料電池の排気ライン２６，３２に接続された燃焼器４０を備え、燃料電池システムの停止時に、改質器への燃料の供給を停止し、水素供給ラインの開閉弁５４を閉弁し、水素分離膜の改質ガス側２１に空気を導入して、水素分離膜の改質ガス側及び透過側２２の水素を除去する。



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【特許請求の範囲】

【請求項１】　水素と酸素又は空気とを反応させることにより発電する燃料電池システムであって、
燃料と空気から改質ガスを生成する改質器と、
該改質器により生成された改質ガスから水素のみを分離する水素分離膜と、
該水素分離膜から精製された水素を燃料電池に供給する水素供給ラインと、
改質器に空気を供給する空気供給ラインと、
燃料電池に酸素又は空気を供給する酸素供給ラインと、
水素分離膜及び燃料電池の排気ラインに接続された燃焼器と、を備え、燃料電池システムの停止時に、改質器への燃料の供給を停止するとともに、水素供給ラインの開閉弁を閉弁し、水素分離膜の改質ガス側に空気を導入することにより、水素分離膜の改質ガス側及び透過側の水素を除去することを特徴とする燃料電池システム。

【請求項２】　水素分離膜の透過側の水素を、水素分離膜の改質ガス側に逆透過させる請求項１に記載の燃料電池システム。

【請求項３】　燃料電池内の水素を、燃料電池システム停止時に、空気で置換する請求項１又は２に記載の燃料電池システム。

【請求項４】　燃料電池の燃料極側と酸素極側との圧力を、ほぼ等しくなるようにした請求項３に記載の燃料電池システム。

【請求項５】　水素と酸素又は空気とを反応させることにより発電する水素分離膜を用いた燃料電池システムの制御方法であって、
燃料電池システムの停止時に、水素分離膜の改質ガス側に空気を導入し、水素分離膜の透過側の水素を水素分離膜の改質ガス側に逆透過させることにより、水素分離膜内の水素を除去することを特徴とする燃料電池システムの制御方法。

【請求項６】　水素と酸素又は空気とを反応させることにより発電する水素分離膜を用いた燃料電池システムの制御方法であって、
燃料電池システムの停止時に、燃料電池内の水素を空気で置換するとともに、水素分離膜の改質ガス側に空気を導入し、水素分離膜の透過側の水素を水素分離膜の改質ガス側に逆透過させることにより、水素分離膜内の水素を除去することを特徴とする燃料電池システムの制御方法。

【請求項７】　燃料電池の燃料極側と酸素極側との圧力を、ほぼ等しくなるように制御した請求項６に記載の燃料電池システムの制御方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】　本発明は、水素分離膜を用いた燃料電池システム及びその制御方法に関する。

【０００２】

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【従来の技術】　現在、開発が進められている燃料電池システムは、水素と、酸素又は空気とを反応させて発電する固体高分子電解質型燃料電池（ＰＥＦＣ）が主に用いられており、通常、燃料電池システムの停止と同時に、燃料電池の発電が停止することが求められている。また、固体高分子電解質型燃料電池の場合、１モルのH_2と１／２モルのO_2とが反応して１モルのH_2Oが生成する。これにより、燃料電池の酸化極側の空気（酸素）と比較して、燃料電池の燃料極側の水素の消費量が大きくなり、燃料電池システムの停止時に、燃料極側の圧力が相対的に大きく低下するため、電解質層を挟む燃料極側と酸化極側との間に大きな圧力差が発生し、燃料電池の電池構成要素が劣化してしまうという問題点があった。

【０００３】　これらの点を解消するため、例えば、特開平７－２７２７４０号公報では、燃料電池システム停止時に、燃料電池内の反応ガス（主に、水素）を不活性ガス（例えば、N_2等）や反応済空気で置換することが開示されており、また、特開平１１－１１１３１９号公報では、不活性ガスの浪費を防止するため、不活性ガスによる置換完了を温度センサーで検知するシステムが開示されている。

【０００４】　また、上記燃料電池で用いる反応ガスは、主成分である水素の濃度が高ければ、高いほど燃料電池の発電効率を向上させることができるだけでなく、被毒作用があるＣＯを除去するため、特開平４－１２１９７３号公報のように、改質ガスを水素分離膜を用いて精製、ＣＯ除去した純水素ガスを燃料電池へ供給するシステムが開示されている。

【０００５】　しかしながら、燃料電池システムに水素分離膜を適用した場合、水素雰囲気下で降温すると、水素分離膜が劣化してしまうため、燃料電池システム停止時に、水素分離膜内から水素を除去する必要があった。このため、従来の燃料電池システム（特開平７－２７２７４０号公報及び特開平１１－１１１３１９号公報参照）に水素分離膜を組み込む場合、水素分離膜の改質ガス側と透過側の両方から水素を除去しなければならないため、燃料電池システムが煩雑になり、コストも高くなるという問題点があった。また、特開平４－１２１９７３号公報では、燃料電池システムの停止と同時に、燃料電池の発電を停止させることについて十分考慮がなされていなかった。

【０００６】

【発明が解決しようとする課題】　本発明は、かかる状況に鑑みてなされたものであり、その目的とするところは、燃料電池システムの停止時に、不活性ガスを用いることなく、水素分離膜の劣化の原因となる水素分離膜内の水素を確実且つ簡便に除去することができるとともに、燃料電池の電池構成要素の劣化を引き起こす燃料電池の両極間の圧力差の発生を抑制することができる水素

分離膜を用いた燃料電池システム及びその制御方法を提供することにある。

【０００７】

【課題を解決するための手段】　即ち、本発明によれば、水素と酸素又は空気とを反応させることにより発電する燃料電池システムであって、燃料と空気から改質ガスを生成する改質器と、該改質器により生成された改質ガスから水素のみを分離する水素分離膜と、該水素分離膜から精製された水素を燃料電池に供給する水素供給ラインと、改質器に空気を供給する空気供給ラインと、燃料電池に酸素又は空気を供給する酸素供給ラインと、水素分離膜及び燃料電池の排気ラインに接続された燃焼器とを備え、燃料電池システムの停止時に、改質器への燃料の供給を停止するとともに、水素供給ラインの開閉弁を閉弁し、水素分離膜の改質ガス側に空気を導入することにより、水素分離膜の改質ガス側及び透過側の水素を除去することを特徴とする燃料電池システムが提供される。このとき、水素分離膜の透過側の水素は、水素分離膜の改質ガス側に逆透過させることが好ましい。

【０００８】　尚、本発明では、燃料電池内の水素を、燃料電池システム停止時に、空気で置換することが好ましく、燃料電池の燃料極側と酸素極側との圧力を、ほぼ等しくなるようにすることが好ましい。

【０００９】　また、本発明によれば、水素と酸素又は空気とを反応させることにより発電する水素分離膜を用いた燃料電池システムの制御方法であって、燃料電池システムの停止時に、水素分離膜の改質ガス側に空気を導入し、水素分離膜の透過側の水素を水素分離膜の改質ガス側に逆透過させることにより、水素分離膜内の水素を除去することを特徴とする燃料電池システムの制御方法が提供される。

【００１０】　更に、本発明によれば、水素と酸素又は空気とを反応させることにより発電する水素分離膜を用いた燃料電池システムの制御方法であって、燃料電池システムの停止時に、燃料電池内の水素を空気で置換するとともに、水素分離膜の改質ガス側に空気を導入し、水素分離膜の透過側の水素を水素分離膜の改質ガス側に逆透過させることにより、水素分離膜内の水素を除去することを特徴とする燃料電池システムの制御方法が提供される。このとき、本発明では、燃料電池の燃料極側と酸素極側との圧力を、ほぼ等しくなるように制御することが好ましい。

【００１１】

【発明の実施の形態】　本発明の燃料電池システムは、燃料電池システムの停止時に、改質器への燃料の供給を停止するとともに、水素供給ラインの開閉弁を閉弁し、水素分離膜の改質ガス側に空気を導入することにより、水素分離膜の改質ガス側及び透過側の水素を除去するものである。これにより、燃料電池システムの停止時に、水素分離膜の劣化の原因となる水素分離膜内の水素を確実且つ簡便に除去することができるとともに、不活性ガスを用いることなく、燃料電池の電池構成要素の劣化を引き起こす燃料電池の両極間の圧力差の発生を抑制することができる。

【００１２】　ここで、本発明の燃料電池システムの主な特徴は、水素分離膜内の水素を除去する際に、水素分離膜の改質ガス側に残存する水素を空気で置換することにより、水素分離膜の改質ガス側の水素分圧を低下させ、水素分離膜の透過側の水素を水素分離膜の改質ガス側に逆透過させることにある。これにより、水素分離膜の透過側にパージラインを設けることなく、水素分離膜の改質ガス側に空気を導入するだけで、降温時における水素分離膜の劣化の原因となる水素分離膜内の水素を確実且つ簡便に除去することができる。

【００１３】　また、本発明の燃料電池システムは、燃料電池システム停止時に、燃料電池内の水素を空気で置換することが好ましい。これにより、燃料電池システム停止時に、燃料電池の発電を直ちに停止することができるだけでなく、燃料電池の電池構成要素の劣化を引き起こす燃料電池の両極（燃料極と酸化極）間の圧力差の発生を抑制することができる。尚、燃料電池の燃料極側と酸素極側との圧力は、ほぼ等しくなるように制御することが好ましい。

【００１４】　更に、本発明の燃料電池システムは、置換用ガスとして、不活性ガスの代わりに空気を用いることが好ましい。これにより、不活性ガスを貯蔵するボンベが不要であるため、燃料電池システムの軽量化及びランニングコストの低減に寄与することができる。

【００１５】　以下、図面に基づき本発明を更に詳細に説明する。図１は、本発明の燃料電池システムの一例を示した概略構成図である。本発明の燃料電池システムの一例は、図１に示すように、燃料と空気から改質ガスを生成する改質器１０と、改質器１０により生成された改質ガスから水素のみを分離する水素分離膜２０と、水素分離膜２０から精製された水素を燃料電池３０に供給する水素供給ライン２４と、改質器１０及び燃料電池３０に空気を供給する空気供給ライン１６，１８と、水素分離膜２０及び燃料電池３０の排気ライン２６，３２に接続された燃焼器４０とを備えたものである。尚、燃焼器４０は、改質燃料と空気との燃焼雰囲気中に、改質器１０、水素分離膜２０及び燃料電池３０からの排気ガスを導入することにより、排気ガス中の余剰な水素や酸素等を処理するものである。また、燃焼器４０への改質燃料供給ライン１４は、必ずしも必要でなく、排気ライン２６から供給される改質ガスの未透過ガスの燃焼により改質器１０の運転温度が保持されれば問題ない。

【００１６】　ここで、上記に示す燃料電池システムは、燃料電池システムを停止させる場合、以下のような手順で行なわれる。まず、燃料供給ライン１２の第１開閉弁５０を閉弁し、改質器１０への燃料供給を停止する

と同時に、水素供給ライン２４の第５開閉弁５４を閉弁し、燃料電池３０への水素供給を停止する。

【００１７】　次に、第４開閉弁５３と第６開閉弁５５を開弁し、改質器１０内及び水素分離膜２０の改質ガス側２１に空気を導入し、改質器１０内の改質ガス、水素分離膜２０内及び燃料電池３０内の水素を空気で置換することにより、改質器１０及び燃料電池３０の機能を停止させる。このとき、水素分離膜２０の改質ガス側２１の水素分圧の低下により、水素分離膜２０の透過側２２の水素は、水素分離膜２０の改質ガス側２１へ逆透過するため、水素分離膜２０内の水素を実質０に近い水素分圧まで除去することができる。尚、改質器１０、水素分離膜２０及び燃料電池３０から排出された排気ガスは、燃焼器４０で燃焼処理された後、系外に排出される。

【００１８】　最後に、第４開閉弁５３、第６開閉弁５５及び第７開閉弁５６を閉弁した後、改質燃料供給ライン１４の第２開閉弁５１と空気供給ライン１６の第３開閉弁５２を閉弁し、燃焼器４０を停止させ、燃料電池システムを降温させる。

【００１９】　尚、それぞれの開閉弁５０～５６、燃料供給ライン１２に接続された燃料ポンプ（図示せず）、改質燃料供給ライン１４に接続された改質燃料ポンプ（図示せず）及び空気供給ライン１６，１８に接続されたコンプレッサ（図示せず）は、電気的に接続され、これらの動作が制御手段（図示せず）でコントロールされている。

【００２０】

【実施例】　以下、本発明を実施例を用いてさらに詳細に説明するが、本発明はこれらの実施例に制限されるものではない。

（実施例）本発明の燃料電池システムにおける水素分離膜内の水素除去方法を検証するため、図２に示す装置を用いて実験を行った。反応管６４（ステンレス製、内容積：０．５ｌ）に水素分離膜６０を設置した後、反応管６４を電気炉６２で４００℃に加熱した。次に、バルブＶ１を開け、マスフローコントローラＭ１を用いて、８気圧（ゲージ圧）、６ｌ／ｍｉｎのメタノール改質模擬ガス（水素：６５％、二酸化炭素：２３％、一酸化炭素：２％、水蒸気１０％）を反応器６４内に供給した。尚、供給ガスラインは、水蒸気が凝縮しないように、リボンヒーターにて１３０℃に加熱した。

【００２１】　このとき、透過水素量は、流量計Ｍ３で測定した結果、３ｌ／ｍｉｎであり、水素回収率は、８０％であった。尚、上記測定時は、バルブＶ１，Ｖ３，Ｖ４が開放状態であった。

【００２２】　更に、図２に示す装置を上記の実験条件で１時間運転した後、バルブＶ４を開けた状態で、バルブＶ１，Ｖ３を閉じ、バルブＶ２を開けて、空気をゲージ圧：０．２気圧、マスフローコントローラＭ２で１０ｌ／ｍｉｎで反応器６４内に導入した。このとき、反応管６４内に空気を導入すると、圧力計Ｐが示すように、水素分離膜６０の透過側の圧力が下がり始め、１ｍｉｎ以内に絶対圧でほとんど０気圧となった。

【００２３】　以上のことから、水素分離膜６０内の水素除去は、水素分離膜６０の改質ガス側の水素分圧を著しく低下させ、水素分離膜６０の透過側に大気圧で残存していた水素ガス（濃度：ほぼ９９％以上）を水素分離膜６０の改質ガス側に逆透過させることにより行われていることを確認した。尚、上記水素分離膜は、外径：１７ｍｍ、長さ：１００ｍｍのアルミナ多孔質基体（細孔径：０．６μｍ）の表面に、メッキ法で５μｍのＰｄ薄膜を成膜したものを用いた。

【００２４】

【発明の効果】　本発明の燃料電池システム及びその制御方法は、燃料電池システムの停止時に、不活性ガスを用いることなく、水素分離膜の劣化の原因となる水素分離膜内の水素を確実且つ簡便に除去することができるとともに、燃料電池の電池構成要素の劣化を引き起こす燃料電池の両極間の圧力差の発生を抑制することができる。

【図面の簡単な説明】

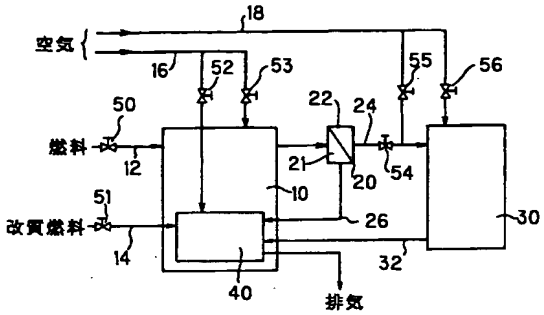
【図１】　本発明の燃料電池システムの一例を示す概略構成図である。

【図２】　本発明の燃料電池システムにおける水素分離膜内の水素除去実験装置の一例を示す概略模式図である。

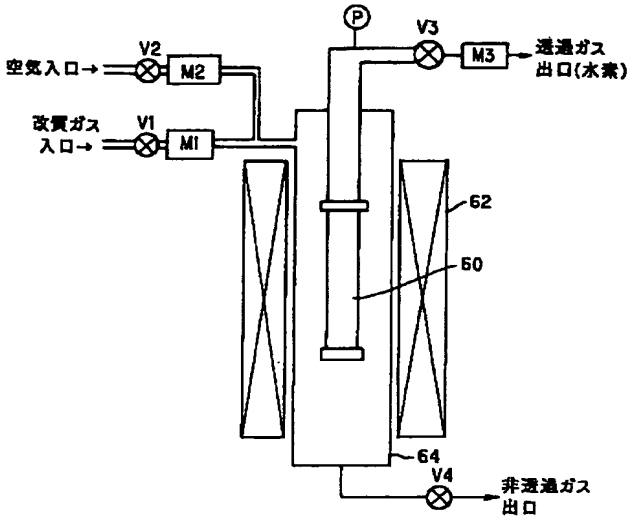
【符号の説明】

１０…改質器、１２…燃料供給ライン、１４…改質燃料供給ライン、１６…空気供給ライン，１８…空気供給ライン（酸素供給ライン）、２０…水素分離膜、２１…改質ガス側（水素分離膜）、２２…透過側（水素分離膜）、２４…水素供給ライン、２６…排気ライン、３０…燃料電池、３２…排気ライン、４０…燃焼器、５０…第１開閉弁、５１…第２開閉弁、５２…第３開閉弁、５３…第４開閉弁、５４…第５開閉弁、５５…第６開閉弁、５６…第７開閉弁、６０…水素分離膜、６２…電気炉、６４…反応管、Ｖ１～Ｖ４…バルブ、Ｍ１～Ｍ２…マスフローコントローラ、Ｍ３…流量計、Ｐ…圧力計。

【図１】



【図２】



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